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More on the relation between the thermal activation energy of the electrical conduction of the organic semiconductors and the first excited singlet state energy of the molecules

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Abstract : The present results are concerned with the dark conduction behaviour of a new series of merocyanine dyes derived from different heterocyclic nuclei in thin-film form on a surface type raster cell The temperature dependence of dark current follows Arrhenius relation An attempt has been made to correlate the thermal activation energy (ΔE_D) and the first excited singlet state energy of the molecules (^1E)

Keywords : Conductivity, activation energy, organic semiconductors

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1. Introduction

In the recent years, a good amount of work has been done to understand the electrical conduction processes in organic solids. This is clear from a look at the books published [1–4]. Despite this effort, the evidence concerning the conduction processes is inconclusive and often contradictory. The electrical properties of conjugated polycyclic molecular solids are related to the number of condensed aromatic rings and to the number of π-electrons in the molecules. Systems such as : naphthalene and anthracene containing a few rings have large energy gaps, low carrier mobilities and consequently high resistivities. Inokuchi *et al* [5] has

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shown that the conductivity increases with the number of π-electrons and the conjugated double bonds in the molecule and the activation energy decreases with the increasing number of π-electrons.

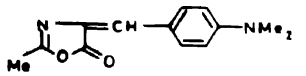
It is well known that in the case of elemental semiconductors, the activation energy for electrical conduction is theoretically expected to be half the band gap. This theoretical result is consistent in magnitude with the experimental observations. In the case of organic semiconductors, the picture is not quite clear. Akamatu and Sano [6] reported that the optical threshold energies for photoconduction were nearly in accord with the large wavelength's edge of optical absorption spectra of crystals and also in agreement with the values of energy gaps which were estimated from the temperature dependence of electrical conductivity. Though, it is accepted that the band structure of an organic substance differs a little from molecular energy levels, it is found that in the case of some substances, there is a good correlation between the activation energy (ΔE_D) and the first excited singlet state energy (^1E) [7–9] and in some compounds no such correlation exists [10–12]. Eley [7] has shown that in the case of small aromatics and nucleosides, there is a similarity between the activation energy and the singlet state energy which suggests that $\Delta E_D = E_G$, where E_G is the energy gap. However, the search for the relation between the spectroscopic data and activation energy continues [13–20].

Narasimharaghavan *et al* [20] reported data on a series of anthraquinone derivatives and shown that there is a correspondence between the thermal activation energy and first excited singlet state energy of the molecules *i.e.* $^1E \approx 7\ \Delta E_D$. In the present paper, we have tried to investigate such relation on a new series of merocyanine dyes (six in number) between the spectroscopic data and activation energy for the dark conduction. The photoconduction and photovoltaic properties of these dyes have been reported elsewhere [21, 22].

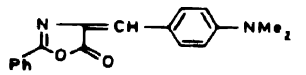
2. Experimental details

A new series of merocyanine dyes was synthesized and purified by soxhelet extraction, repeated recrystallization and finally by column chromatography. They are para-dimethylamino benzylidiene dyes derived from six different heterocyclic nuclei : 2-methyl oxazolone (Dye I), 2-phenyl oxazolone (Dye II), 1-phenyl-3-methyl pyrazolone (Dye III), chroman-2,4-dione (Dye IV), 3-phenyl iso-oxazolone (Dye V) and N-methyl rhodanine (Dye VI). Their structures are shown in Figure 1.

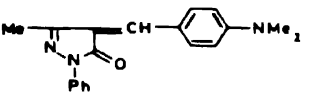
The d.c. conductivity measurements of these compounds were carried out on a raster type surface cell [23] (Figure 2) which has 35 gaps of 0.02 cm width in each, prepared by etching out pure aluminium (BDH, UK, 99.99% pure) coated on a previously cleaned transparent quartz plate by vacuum sublimation technique in the vacuum of the order of 10^{-4} Torr. The conductivity was measured at different applied potentials in the range of 0–200 V and at different temperatures between 288 K–333 K. The samples could not be studied beyond 333 K as they started deforming and the measurements were not consistent. The conductivity studies have been made in air. The details of experimental set-up has been reported elsewhere [23–25].



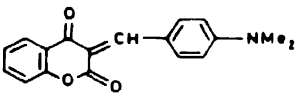
PDAB-2-Methyloxazolone (DYE I)



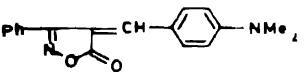
PDAB-2-Phenyloxazolone (DYE II)



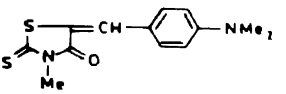
PDAB-1-Phenyl – 3 – Methylpyrazolone (DYE III)



PDAB-Chroman-2,4-Dione (DYE IV)

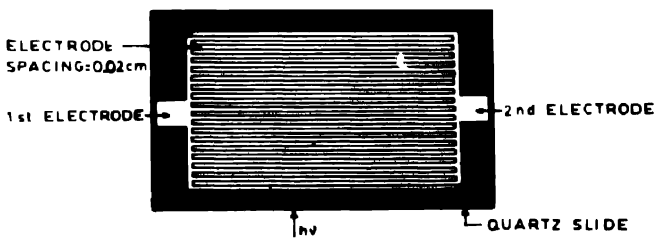


PDAB-3-Phenyl Isooxazolone (DYE V)



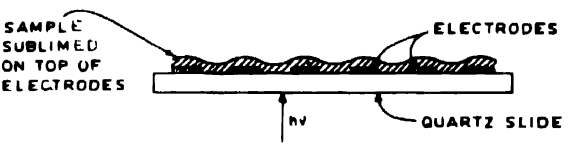
PDAB-N-Methyl Rhodanine (DYE VI)

Figure 1. Structures of the dyes studied



(a)

CROSS-SECTIONAL VIEW OF (a) WITH FEW ELECTRODES



(b)

Figure 2. Surface type cell arrangement of the electrodes used in the study.

The absorption spectra were recorded on a Perkin-Elmer Lambda 4B UV/VIS Spectrophotometer in thin film form and also in n-hexane which is a non-polar solvent. Saturated hydrocarbon solvents (n-hexane, cyclohexane *etc*) are said to be good spectroscopic solvents because they have comparatively low refractive indices and dielectric constants and hence give spectra nearly resembling the solid state and vapor spectra [26]. A procedure to calculate the photon energy [27] corresponding to the higher wavelength's edge of the absorption spectra was adopted.

3. Results and discussion

Dark current has been studied as a function of temperature for different fixed voltages. Readings have been taken in increasing runs of temperature after annealing the samples. The dark current was found to follow Arrhenius relation,

$$I_D = A \exp(-\Delta E_D / kT)$$

where A is a pre-exponential factor, ΔE_D is the thermal activation energy of the dark conduction, k is Boltzmann constant and T is absolute temperature of the sample. Figure 3 shows a typical log I_D *vs* $1/T$ plot for all dyes at a fixed voltage of 150 V. Single activation energies have been observed which vary by a small value with applied voltage in the case of

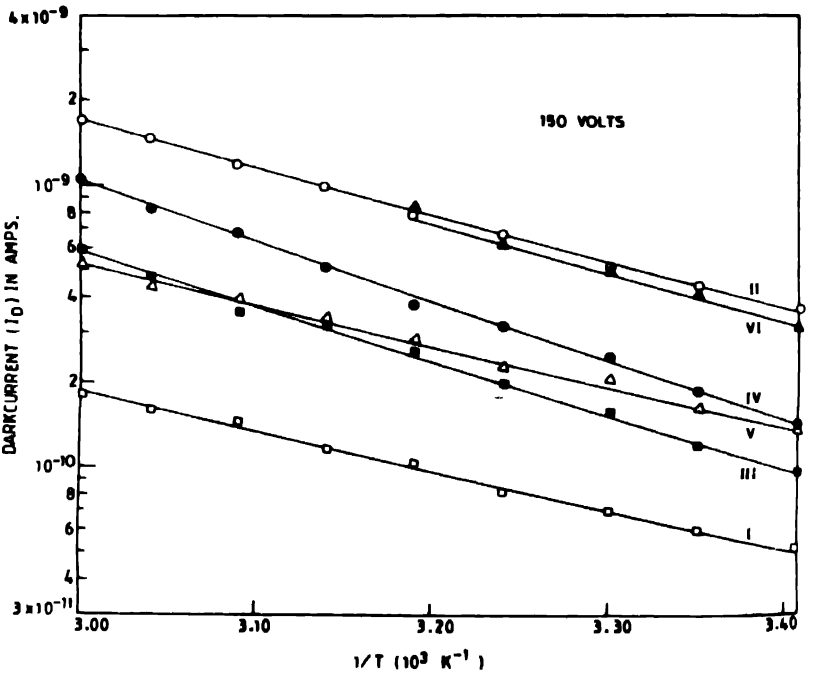


Figure 3. A plot between the log I_D *vs* $1/T$

Dyes I, III and IV. The value of ΔE_D was calculated from the slope of the plot of log I_D *vs* $1/T$ ($k = 8.616 \times 10^{-5}$). The relatively lower values of activation energies do suggest that an

extrinsic process is dominant [28, 29] and charge carriers are released from the traps. The activation energy values were found to decrease by a very small value with applied voltage.

These dyes behave as p-type semiconductors which is shown below in view of their conductivity in air. Hence, the charge carriers are holes and these are created by the promotion of electrons from the valence band to the traps in the band gap. There has been a marked difference in the dark current and the thermal activation energies of the dyes in air and vacuum [24]. The injection of the charge carriers in the organic solids in ambient atmosphere has been reported [30] and in the present case also it can be attributed to the ambient. There has been two orders increase in the magnitude of the dark current when ambient conditions were changed from vacuum to air. This result goes hand in hand with the Meier's classification [31] of vacuum and oxygen semiconductors. The maximum values of dark current observed for the dyes from Dye I to Dye VI are 0.257, 2.130, 0.722, 1.190, 0.698 and 3.480 nanoamps. respectively.

The photon energy corresponding to the higher wavelength's edge of the absorption maxima of these dyes was taken as the energy of the first excited singlet state energy (^1E). For the present series of dyes, the value of ΔE_D is far lower than ^1E. Figure 4 shows the plot of activation energy (ΔE_D) and the first excited singlet state energy (^1E). The dye numbers represent the particular merocyanine dye in Figure 4. It is clear from the figure that all the dyes fall on the line $^1E \approx 3\ \Delta E_D$ except Dyes I and IV which is in the contradiction to the

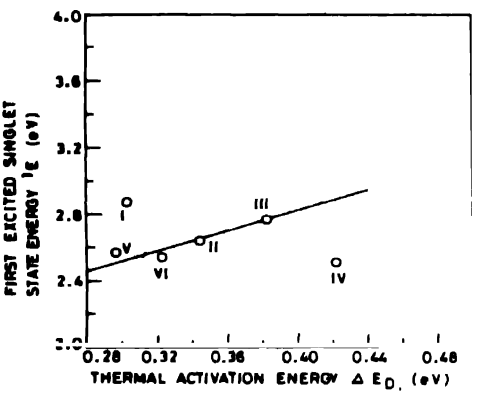


Figure 4. A plot between the thermal activation energy (ΔE_D) for dark conduction *vs* the first excited singlet state energy (^1E).

results published so far. Here, it is worth noting that Dyes I, III and V which are less conductive, have an activation energies of 0.303, 0.382 and 0.296 eV's and Dye I has the highest value of ^1E. The activation energy is approximately 1/3 of the first excited singlet state energy. The substitution of phenyl ring in Dye II results in higher conduction. In Dye VI, higher conduction is observed, may be because of sulfur atoms which normally favour conduction. Methyl group at nitrogen atom enhances conductivity compared to that of phenyl group at nitrogen atom [32] which has been observed in the case of Dyes III and VI. In all cases ^1E shifts bathochromically as expected.

As is known, the activation energy indicates the depth of traps in the energy band gap in the case of the extrinsic semiconductors which is clear from the compounds understudy. Under these facts, if any correlation exists between ΔE_D and ^1E in the present series of dyes, we can say that the possible correlation is $^1E \approx 3\ \Delta E_D$.

4. Conclusion

Summarily we can state that :

1. The observed lower values of the thermal activation energy of dark conduction do suggest that the extrinsic process of charge carrier transport is involved. These values do not correspond to the band gap energy, but to the depth of traps.
2. If $^1E \approx 3\ \Delta E_D$ can not be accepted as a correlation, we can say that there is a correspondence between the thermal activation energy (trap depth in our case) and the first excited singlet state energy of the molecule.

Acknowledgments

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